

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
 International Bureau



(43) International Publication Date
 25 April 2002 (25.04.2002)

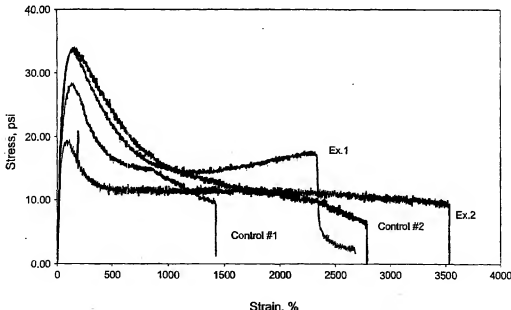
PCT

(10) International Publication Number
 WO 02/32994 A2

- (51) International Patent Classification: C08L 23/22, 23/28, 21/00
- (21) International Application Number: PCT/US01/31620
- (22) International Filing Date: 11 October 2001 (11.10.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/688,425 16 October 2000 (16.10.2000) US
- (71) Applicant (for all designated States except US): EXXON-MOBIL CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).
- (72) Inventors; and
 (75) Inventors/Applicants (for US only): TSE, Mun, Fu [US/US]; 1706 Fair Oaks Drive, Seabrook, TX 77586 (US); WANG, Hsien-Chang [US/US]; 536 College, Bel-laire, TX 77401 (US); KRISHNAMOORTI, R. [US/US]; 2412 Yorktown #312, Houston, TX 77056 (US); TSOU, Andy, H. [US/US]; 3007 Prairie Knoll Court, Houston, TX 77059 (US).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published: — without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: POLYMER BLEND COMPATIBILIZATION USING ISOBUTYLENE-BASED BLOCK COPOLYMERS



(57) Abstract: Compatibilized blends of an isobutylene polymer and an unsaturated diene polymer are prepared using a compatibilizing agent comprising a block-graft copolymer containing polyisobutylene segments and C₆ to C₈ alkyl-substituted styrene polymer segments, such as poly(t-butylstyrene) segments.

WO 02/32994 A2



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

POLYMER BLEND COMPATIBILIZATION USING
ISOBUTYLENE-BASED BLOCK COPOLYMERS

FIELD OF THE INVENTION

5 The present invention relates to compatibilized blends comprising high and low unsaturation elastomers.

BACKGROUND

10 Vulcanizates based on blends of little-or-no-olefinic-unsaturation elastomers with more highly unsaturated elastomers are of interest in the rubber industry primarily because of their special properties, e.g., superior resistance to ozone degradation and consequent cracking, improved resistance to chemical attack, improved temperature stability and unique dynamic response. These blends permit synergy between the individual elastomers, yielding composite
15 blend property combinations unattainable in the individual elastomers. But these desirable properties occur only when an intimate homogeneous blend of the elastomers with phase sizes of less than 5 microns, generally 1 micron or less, is produced and maintained in the blend, and a satisfactory interfacial adhesion level is achieved.

20 Unfortunately, it is generally known that most polymers are not compatible with one another unless specific, favorable interactions are present, because the favorable entropy of mixing is too small to overcome the unfavorable enthalpy of mixing, making mixing disfavored. Blends produced by normal techniques are grossly inhomogeneous with phase sizes many microns in
25 diameter. This gross incompatibility of the individual polymers with a consequent inability to produce and maintain desired homogeneous, fine phase sizes is particularly evident when the individual polymers differ considerably in solubility parameters. That is the case when low unsaturation elastomers are blended with the more highly unsaturated elastomers.

30 Another problem with saturated-unsaturated elastomer mixtures is that, even if high-shear mixing produces intimate dispersions, afterwards the mixtures phase-separate into blends that are grossly inhomogeneous with the individual

phase sizes many microns in diameter. These grossly inhomogeneous blends generally have very poor property combinations, usually much worse than the individual polymers, rather than displaying the desired property combinations that come from intimate homogeneous blends with phase sizes less than 5 microns. generally 1 micron or less.

One approach towards compatibilizations of non-compatible polymers is to blend in a block copolymer that contains one chain segment derived from monomers compatible with a blend polymer and another chain segment derived from monomers compatible with another blend polymer. For example, EP 691378A discloses polymer blends comprising a polycarbonate resin and polyisobutylene that are compatibilized by including a minor amount of a polycarbonate-polyisobutylene block copolymer in the blend composition. In addition, U.S. Patent No. 5,741,859 discloses block copolymers of polyisobutylene and polydimethylsiloxane and suggests their use as compatibilizers.

Di, tri and radial block copolymers containing polyisobutylene and poly(p-chlorostyrene) are disclosed as compatibilizers by *Kennedy et al.* in Polym.Mater.Sci.Eng., 63, p 371-375, 1990.

Polymer blends comprising a mixture of an isobutylene polymer and a more highly unsaturated elastomer such as polybutadiene or polyisoprene are potentially ozone resistant, chemical resistant, air tight, and temperature stable as described above. But isobutylene polymers such as polyisobutylene, copolymers of isobutylene with isoprene (butyl rubber), copolymers of isobutylene with a para-alkylstyrene, and their halogenated versions are not compatible with more highly unsaturated elastomers such as polymers based on conjugated diene monomers. In the absence of specific, strong chemical interactions, these dissimilar polymers have a positive free energy of mixing and hence are thermodynamically incompatible because the heat of mixing is usually positive and the entropy gained upon mixing these dissimilar polymeric molecules is small. The result is high interfacial tension and poor adhesion between the two blend phases and weak blend mechanical properties due to the lack of a highly structured morphology. The present invention is directed towards an improved

blend of high and low unsaturation elastomers by the incorporation of a block copolymer.

SUMMARY

5 The invention provides a compatibilized polymer blend comprising:

(a) an isobutylene polymer selected from polyisobutylene, random copolymers of isobutylene with up to 10 weight % isoprene, halogenated random copolymers of isobutylene with up to 10 weight % isoprene, random copolymers of isobutylene with up to 20 weight % of a para-alkylstyrene, halogenated random
10 copolymers of isobutylene and up to 20 weight % of a para-alkylstyrene and their mixtures;

(b) at least one olefinically unsaturated diene polymer; and

(c) a compatibilizer for components (a) and (b) comprising a block copolymer of at least one recurring polyisobutylene segment and at least one
15 recurring segment comprising a C₄-to-C₆ alkyl-ring-substituted styrene or ring-substituted alpha-methylstyrene.

Some compatibilizers comprise a di, tri or radial block copolymer of polyisobutylene and para-tertiary-butylstyrene (tbS).

The invention also provides for co-vulcanized elastomer compositions
20 based on these blends.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of tensile stress-strain measurements of polymer blends prepared in the examples;

25 Figure 2 is a plot of dynamic thermal mechanical measurements of one polymer blend prepared in the examples; and

Figure 3 is another plot of dynamic thermal mechanical measurements of another polymer blend prepared in the examples.

DETAILED DESCRIPTION

The compatibilizer copolymers useful in accordance with this invention are block copolymers containing at least one polymer chain segment derived from a C₄-to-C₆-alkyl-substituted styrene or alpha-methylstyrene and at least one polymer chain segment derived from isobutylene. These materials may comprise S-iB-S or iB-S-iB triblock copolymers, S-iB diblock copolymers, (S-iB)_n multiblock copolymers, graft copolymers of poly S or a poly iB backbone, or star-branched polymers containing poly S and poly iB segments, in which iB is isobutylene and S is a C₄-to-C₆-alkyl-substituted styrene or alpha-methylstyrene. For the purposes of this invention, all of these materials will be referred to as block-graft copolymers.

The styrenic part of the block-graft copolymer comprises one or a mixture of styrene or alpha-methylstyrenes that are ring-substituted at the ortho, meta, or para position with a linear or branched, C₄ to C₆ alkyl group. Some embodiments select the styrenic monomer as para-t-butylstyrene.

Some invention block copolymers have a GPC number average molecular weight in the range of 10,000 to 500,000, others 50,000 to 200,000. In some embodiments, the styrenic monomer segment(s) comprise at least 10 weight % of the copolymer and the balance of the polymer comprises isobutylene segments. Some embodiments select block-graft copolymers as S-iB-S or iB-S-iB tri-block copolymers containing 10-50 weight % of the styrenic block copolymer segments. Other embodiments select the copolymers similarly with between 10 and 30 weight % of the styrenic block copolymer segments.

These block-graft copolymers are well known in the art and can be prepared by living, carbocationic, sequential polymerization using a catalyst comprising a tertiary alkyl halide, a tertiary aralkyl halide, or a polymeric halide initiator and a methyl aluminum or methyl boron compound containing co-initiator. Polymerization is conducted in a suitable solvent as is known in the art such as anhydrous methylene chloride, hexane, or mixed solvents. Typical polymerization temperatures are below -30°C. Some embodiments select the

polymerization temperature to be below -60°C. These polymerization methods are more completely disclosed in U.S. Patent Nos. 4,946,899, 5,506,316 and 5,451,647.

5 Invention polymer blends are characterized as having at least two components: an olefinically unsaturated diene polymer component and an isobutylene component. The unsaturated diene component includes elastomeric conjugated diene (diolefin) polymers such as polybutadiene, natural rubber, synthetic polyisoprene, copolymers of butadiene with up to 40 weight % of styrene or acrylonitrile, polychloroprene, and their mixtures. Some embodiments
10 select the olefinically unsaturated component as polybutadiene or polyisoprene. The unsaturated polymer may also be non-elastomeric and may include liquid-to-waxy polybutadiene or butadiene copolymers having a number average molecular weight in the range of 300 up to 10,000.

The isobutylene polymer blend component includes polyisobutylene, random copolymers of isobutylene with up to 10 weight % of isoprene (butyl rubber), chlorinated or brominated butyl rubber containing from 0.3 to 3 weight % halogen, random isobutylene copolymers with up to 20 weight %, and up to 14 weight % of para-alkylstyrene such as para-methylstyrene (PMS) and chlorinated or brominated iBPMS copolymers containing from 0.1 to 10 mol% of
20 halomethylstyrene groups. For halogenated iBPMS, the halogen is present as benzylic halogen on the polymer molecules. The iBPMS and halogenated iBPMS copolymers are more particularly described in U.S. Patent No. 5,162,445.

Inventor blends generally contain the isobutylene polymer and olefinically unsaturated polymer at 95-5 parts by weight of isobutylene polymer per 5-95 parts
25 by weight of unsaturated polymer, respectively. Some inventor blends generally contain the isobutylene polymer and olefinically unsaturated polymer at 50-10 parts by weight of isobutylene polymer per 10-50 parts by weight of unsaturated polymer, respectively. The block-graft copolymer additive may be present at between 2 to 20 weight %, although some embodiments select this additive at
30 between 5 to 15 weight %, based on the blend polymer content.

It is surprising that the block-graft copolymers containing polyisobutylene and poly(p-tertiary-butylstyrene) segments will compatibilize blends containing

highly unsaturated elastomers such as polybutadiene or polyisoprene, because the block-graft copolymer does not contain a diene polymer segment. It is unexpected that the styrenic polymer segments serve to compatibilize such elastomeric dienes.

5 The block-graft copolymers may contain from 10 to 90 weight % of the styrenic polymer segments, or from 10 to 50 weight % of the styrenic polymer segments, with the balance being polyisobutylene segments. For triblock block-graft copolymers, the styrenic segments may form the outer blocks (S-iB-S) the inner block iB-S-iB. In blends containing high isobutylene polymer amounts, e.g.
10 greater than 65 weight %, iB-S-iB type block-graft copolymers can serve as compatibilizers. In blends containing higher unsaturated diene polymer levels, e.g. greater than 65 weight %, S-iB-S type block-graft copolymers can serve as compatibilizers. Some block-graft copolymer embodiments contain styrenic polymer segments having a GPC number average molecular weight of at least
15 5,000, some from 10,000 to 50,000, and some from 10,000 to 30,000.

Invention blend composition can be vulcanized and shaped to form useful articles such as tire sidewalls, tire treads, tire carcasses, tire linings, hoses, belts, mechanical goods, and similar articles.

Suitable vulcanizing or cross-linking methods include exposing the
20 composition to high energy radiation (ultra violet, electron-beam, or gamma) or adding a suitable peroxide or accelerated sulfur vulcanizing system into the composition.

Examples of suitable peroxides include dialkyl peroxides, ketal peroxides, aralkylperoxides, peroxyethers, and peroxyesters. Some embodiments restrict
25 peroxides to di-cumylperoxide, di-tert-butylperoxide, benzoyl peroxide, tert-butylperbenzoate, and similar known free radical generators. The quantity of peroxide generally ranges from 1 to 10 parts by weight, although some embodiments select peroxide at 1.5 to 6 parts by weight per 100 parts by weight of curable polymer.

30 Accelerated sulfur vulcanization systems that function as curatives in the present invention include sulfur or mixtures of sulfur and sulfur-containing accelerators and/or phenol-formaldehyde resins. Suitable accelerators include

benzothiazyl disulfide, N-oxydiethylene benzothiazole-2-sulfenamide, 2-mercaptobenzothiazole, alkyl phenol disulfides, alkylthiuram sulfides, m-phenylenebismaleimide, N,N'-diarylguanidines, dialkyl and diaryl-dithiocarbamates, and similar materials.

5 Suitable dialkyldithiocarbamates include the dialkyldithiocarbamates of zinc, bismuth, cadmium, copper, lead, selenium, and tellurium in which the alkyl group contains from 1 to 5 carbon atoms, piperidinium pentamethylenedithiocarbamate, and their mixtures.

10 Suitable diaryldithiocarbamates include the diaryldithiocarbamates of zinc, bismuth, cadmium, copper, lead, selenium, tellurium, and their mixtures.

 Suitable alkylthiuram sulfides include dipentamethylene thiuram tetrasulfide, tetrabutylthiuram disulfide, tetraethylthiuram disulfide, tetramethylthiuram monosulfide, tetrabenzylthiuram disulfide, and their mixtures.

15 Sulfur and vulcanization accelerators are normally added to the composition at 0.5 to 8 parts by weight based on 100 parts by weight of curable elastomer. The accelerated sulfur curing system is sometimes used as a cocurative in curing systems also containing zinc oxide, or an equivalent, as an auxiliary curative agent. Zinc oxide is normally used in such systems at 0.2 to 7 parts by weight per 100 parts by weight of elastomer.

20 The elastomer composition may also contain other additives such as scorch retarders, lubricants, fillers, plasticizers, tackifiers, coloring agents, blowing agents, and antioxidants, provided that these do not prevent with curing.

25 Examples of fillers include inorganic fillers such as reinforcing grade carbon black, silica, calcium carbonate, talc, and clay, and organic fillers such as high-styrene resin, coumarone-indene resin, phenolic resin, lignin, modified melamine resins, and petroleum resins.

30 Examples of lubricants include petroleum-type lubricants such as oils, solid and liquid paraffins, coal-tar-type lubricants such as coal tar and coal tar pitch; waxes such as beeswax, carnauba wax, and lanolin; and synthetic polymeric substances such as petroleum resins.

Examples of plasticizers include hydrocarbon oils, e.g., paraffin, aromatic, and naphthenic oils, phthalic acid esters, adipic acid esters, sebacic acid esters, and similar plasticizers.

Examples of tackifiers are petroleum resins, coumarone-indene resins, terpene-phenol resins, and xylene/formaldehyde resins.

Examples of coloring agents are inorganic and organic pigments.

Examples of blowing agents are sodium bicarbonate, ammonium carbonate, N-N'-dinitrosopenta-methylenetetramine, azocarbonamide, azobisisobutyronitrile, benzenesulfonyl hydrazide, toluenesulfonyl hydrazide, p-toluenesulfonyl azide, urea, and the like.

The vulcanizable composition may be prepared and blended using solvent blending or any suitable melt-mixing device such as an internal mixer (Braebender Plasticorder), a Banbury Mixer, an extruder, a mill mixer, a kneader, or a similar mixing device. Blending temperatures and times in these melt-mixing devices may range from 100°C to 200°C and from 1 to 15 minutes, respectively. Sometimes the polymer components are subjected to high shear or extensional mixing to form an intimate homogeneous blend having a dispersed phase with a phase size of less than 5 microns. Some embodiments prepare the phase size less than 2 microns.

EXAMPLES

The following examples illustrate the invention.

The block copolymer used in Examples 1 and 2 was synthesized via living carbocationic polymerization using an aluminum-based initiator. Values of weight % (Wt %), end block, and number-average molecular weight, M_n , of this triblock copolymer are shown:

<u>Designation</u>	<u>Wt % End Block</u>	<u>$M_n \times 10^{-3}$</u>
12tbS-80iB-12tbS	23% tbS	12-80-12

where tBS is tertiary-butylstyrene and iB is isobutylene. As an example, the isobutylene-based polymer used in this invention was a poly(isobutylene-co-4-methylstyrene), abbreviated by PIMS. This copolymer contains 96.25 mol% isobutylene and 3.75 mol% PMS. GPC M_n and M_w are 173,000 and 479,000, respectively. Two diene polymers were used. Budene® 1207 (Goodyear Tire and Rubber Company, Akron OH) is a polybutadiene containing approximately 98% cis-1,4 content, and Natsyn® 2200 1207 (Goodyear Tire and Rubber Company, Akron OH) is a polyisoprene containing 92% (minimum) cis-1,4 content. Four blends were prepared by mixing in toluene followed by extensive drying in a vacuum oven:

Examples 1 and 2 (Ex. 1 and Ex. 2) in Table 1 (numbers expressed in parts by weight) are blends containing the block copolymer compatibilizer and control examples 1 and 2 (Cont. 1 and Cont. 2) do not.

Table 1

	Ex. 1	Ex. 2	Cont. 1	Cont. 2
PIMS	7.27	7.27	8	8
Budene® 1207	7.27	-	8	-
Natsyn® 2200	-	7.27	-	8
tBS-iB-tBS	1.45	1.45	-	-
Irganox® 1010	0.16	0.16	0.16	0.16
Strain at break, %	2700	3500	1400	2800
Max. Stress near Break, psi	18	10	10	7

where Irganox 1010 is a stabilizer (Ciba Geigy).

Tensile stress-strain measurements were performed on these four blends using micro-dumbbell specimens at a test temperature of 25°C and an Instron cross-head speed of 2"/min (ASTM D-1708). As shown by Figure 1, the incorporation of tBS-iB-tBS into PIMS/Budene® 1207 and PIMS/Natsyn® 2200 blends increases the strain at break and the maximum stress near the break point. Dynamic thermal mechanical measurements using 1 Hz frequency and 2°C/min heating rate were also performed on these four blends to determine how tBS-iB-

tbS affects the phase behavior. These measurements are known to those skilled in the art and commonly used. Figures 2 and 3 show the loss tangent (δ) as a function of temperature for the PIMS/Budene® 1207 blend and the PIMS/Natsyn® 2200 blend, respectively. The block copolymer forms a diffused interface between PIMS and the diene polymer as indicated by the increased loss tangent values between the two loss tangent peaks (Figure 2) or by a narrowing of the loss tangent peak (Figure 3).

Additional blends having the composition shown in Table 2 (numbers expressed in parts by weight) were prepared by melt blending. Several 25/75 by weight blends of PIMS/Budene® 1207 and PIMS/Natsyn® 2200 with and without 12TBS-80iB-12TBS were prepared. This blending was carried out in a Braebender mixer at a temperature of 180°C and a rotor speed of 60 rpm for 10 minutes. Each composition in Table 2 was compression-molded at 180°C for 30 minutes to make pads of thickness 0.08". Tensile stress-strain measurements were performed on these molded pads (stored under ambient conditions for 24 hours prior to tests). Micro-dumbbell specimens were used (test temperature 25°C; Instron cross-head speed 2"/minute, using ASTM D1708).

The morphological change of the blends due to the block copolymer was also studied by atomic force microscopy (AFM) measurements. All specimens were AFM analyzed within 8 hours after cryofacing to prevent specimen relaxation. During cryofacing, the specimens were cooled to -150°C and cut with diamond knives in a cryogenic microtome. They were then warmed to ambient temperature in a desiccator under flowing dry nitrogen to avoid atmospheric moisture condensation. Finally, the faced specimens were mounted in a miniature steel vise for AFM analysis. The AFM measurements were performed in air using a rectangular, Si cantilever. AFM phase images of all specimens were processed and measured to compute sizes and shapes of dispersed phases.

As shown in Table 2, incorporating tbS-iB-tbS polymer in the PIMS/Budene® 1207 blend (Ex. 3) increases the strain at break and the maximum stress near the break point over the control composition 3. Incorporating tbS-iB-tbS in the PIMS/Natsyn® 2200 blend (Ex. 4) increases the strain at break over the control composition 4.

Table 2

	Cont. 3	Cont. 4	Ex. 3	Ex. 4
PIMS	4	4	3.64	3.64
Budene 1207	12	-	10.91	-
Natsyn 2200	-	12	-	10.91
tbS-iB-tbS	-	-	1.45	1.45
Irganox 1010	0.16	0.16	0.16	0.16
Strain at Break, %	395	510	560	640
Max. Stress near Break, psi	30	2	64	2
D_n , μm	1.53	0.57	0.83	0.25
D_w , μm	2.17	0.91	1.24	0.32
D_a , μm	2.70	1.15	1.59	0.40
D_v , μm	3.03	1.28	1.86	0.46
F	0.80	0.82	0.74	0.71

D_n = equivalent number-average diameter

D_w = equivalent weight-average diameter

D_a = equivalent area-average diameter

D_v = equivalent volume-average diameter

F = form factor = $4\pi(\text{area})/(\text{perimeter})^2$, a measure of surface irregularities; a smaller F means a higher degree of surface irregularities

Using AFM measurements and image analysis (Photoshop® 5.0, Adobe Systems, Inc.), the PIMS minor phase was characterized by various average diameters, D_n , D_w , D_a , and D_v . The compatilizing effect of tbS-iB-tbS on the PIMS/Budene® 1207 and PIMS/Natsyn® 2200 blends in reducing the size of the PIMS minor phase is obvious based on the Table 2 data. Also, in the presence of tbS-iB-tbS, the PIMS phase size is reduced more in the PIMS/Natsyn® 2200 blend than in the PIMS/Budene® 1207 blend. This is consistent with the observation that the tbS homopolymer is more compatible with polyisoprene than with polybutadiene. The observed form factor lowering in both blends containing tbS-iB-tbS reflects more non-spherical and higher-surface-area PIMS domains. This increase in domain surface area per unit volume indicates a steric stabilization to retard PIMS phase coalescence and/or a reduction in interfacial tension in these blends due to the presence of tbS-iB-tbS compatibilizer.

What is claimed is:

1. A compatibilized polymer blend comprising:
 - a) an isobutylene polymer selected from the polyisobutylene,
5 random copolymers of isobutylene with up to 10 weight % isoprene,
halogenated random copolymers of isobutylene with up to 10 weight %
isoprene, random copolymers of isobutylene with up to 20 weight % of a
para-alkylstyrene, halogenated random copolymers of isobutylene and up
to 20 weight % of a para-alkylstyrene and their mixtures;
 - 10 b) at least one olefinically unsaturated diene polymer; and
 - c) a compatibilizer for components (a) and (b) comprising a block-
graft copolymer of at least one recurring polyisobutylene segment and at
least one recurring segment comprising a C₄-to-C₆alkyl-ring-substituted
styrene or ring-substituted alpha-methylstyrene.
- 15 2. The composition of claim 1 wherein the compatibilizer comprises a
copolymer of isobutylene and para-t-butylstyrene.
3. The composition of claim 2 wherein the compatibilizer comprises a tbS-iB
20 diblock copolymer or a tbS-iB-tbS or iB-tbS-iB triblock copolymer having
a GPC number average molecular weight of 10,000 to 500,000 and that
contains at least 10 weight % of para-t-butylstyrene.
4. The composition of claim 1 wherein the components (a) and (b) are
25 present at 95-5 parts by weight of (a) per 5-95 parts by weight of (b).
5. The composition of claim 4 wherein the compatibilizer is present in the
composition at 2 to 20 weight % based on the blend polymer content.
- 30 6. The composition of claim 3 wherein the compatibilizer is a tbS-iB diblock
or tbS-iB-tbS triblock copolymer having a GPC number average molecular
weight of from 50,000 to 200,000.

7. The composition of claim 1 wherein the isobutylene polymer (a) comprises a copolymer of isobutylene and para-methylstyrene.
- 5 8. The composition of claim 7 wherein the isobutylene polymer (a) is a halogenated copolymer of isobutylene and para-methylstyrene containing benzylic chlorine or bromine.
9. The composition of claim 1 wherein the olefinically unsaturated diene polymer is an elastomer selected from polybutadiene, synthetic polyisoprene, natural rubber, elastomeric copolymers of butadiene with styrene or acrylonitrile, polychloroprene, or their mixtures.
- 10 10. A polymer blend wherein the composition of Claims 1-9 is vulcanized, cured, or cross-linked.
- 15 11. A compatibilized polymer blend comprising:
- a) an isobutylene polymer selected from polyisobutylene, random copolymers of isobutylene with up to 10 weight % isoprene, halogenated random copolymers of isobutylene with up to 10 weight % isoprene, random copolymers of isobutylene with up to 20 weight % of a para-methylstyrene, halogenated random copolymers of isobutylene and up to 20 weight % of a para-methylstyrene or their mixtures;
- 20 b) at least one olefinically unsaturated diene polymer selected from polybutadiene, synthetic polyisoprene, natural rubber, elastomeric copolymers of butadiene with styrene or acrylonitrile, polychloroprene, or their mixtures; and
- 25 c) a compatibilizer for components (a) and (b) comprising a block-graft copolymer of at least one recurring polyisobutylene segment and at least one recurring segment comprising para-l-butylstyrene.
- 30

12. The composition of claim 11 wherein the compatibilizer comprises a tBS-iB diblock copolymer or a tBS-iB-tBS or iB-tBS-iB triblock copolymer having a GPC number average molecular weight of 10,000 to 500,000 and that contains at least 10 weight % of para-t-butylstyrene.
- 5 13. The composition of claim 11 wherein components (a) and (b) are present at 95-5 parts by weight of (a) per 5-95 parts by weight of (b).
14. The composition of claim 13 wherein the compatibilizer is present at 2 to
10 20 weight % based on the blend polymer content.
15. The composition of claim 1 wherein the compatibilizer is a tBS-iB diblock or tBS-iB-tBS triblock copolymer having a GPC number average molecular weight of 50,000 to 200,000.
- 15 16. The composition of claim 11 wherein the isobutylene polymer (a) comprises a copolymer of isobutylene and para-methylstyrene.
17. The composition of claim 16 wherein the isobutylene polymer (a) is a
20 halogenated copolymer of isobutylene and para-methylstyrene containing benzylic chlorine or bromine.
18. The composition of claim 11 wherein the olefinically unsaturated diene polymer is an elastomer selected from polybutadiene, synthetic polyisoprene, natural rubber, elastomeric copolymers of butadiene with
25 styrene or acrylonitrile, polychloroprene, or their mixtures.
19. A polymer blend wherein the composition of Claims 11-18 is vulcanized, cured, or cross-linked.
- 30 20. A compatibilized polymer blend comprising:

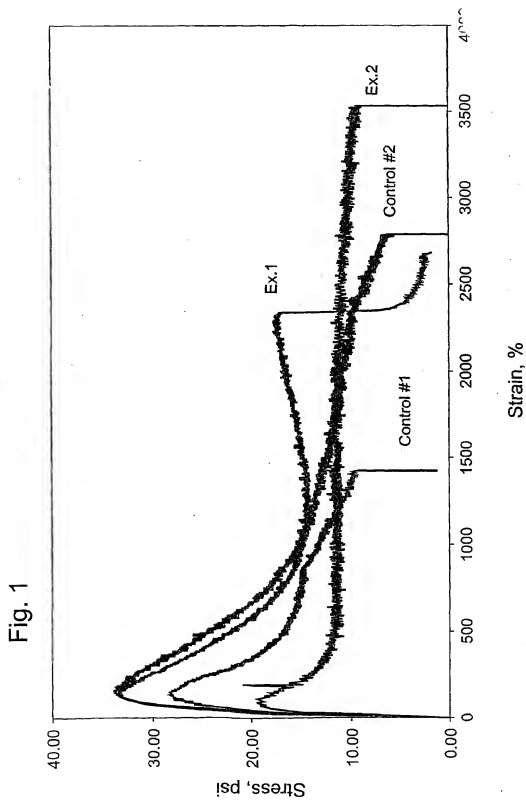
- 5 a) an isobutylene polymer selected from polyisobutylene, random copolymers of isobutylene with up to 10 weight % isoprene, halogenated random copolymers of isobutylene with up to 10 weight % isoprene, random copolymers of isobutylene with up to 20 weight % of a para-alkylstyrene, halogenated random copolymers of isobutylene and up to 20 weight % of a para-alkylstyrene or their mixtures;
- b) at least one olefinically unsaturated diene polymer; and
- 10 c) a compatibilizer comprising a copolymer of isobutylene and para-t-butylstyrene, wherein the compatibilizer comprises a tBS-iB diblock copolymer or a tBS-iB-tBS or iB-tBS-iB triblock copolymer having a GPC number average molecular weight of 10,000 to 500,000 and that contains at least 10 weight % of para-t-butylstyrene.
- 15 21. The composition of claim 20 wherein said components (a) and (b) are present at 95-5 parts by weight of (a) per 5-95 parts by weight of (b).
22. The composition of claim 21 wherein the compatibilizer is present at 2 to 20 weight % based on the blend polymer content.
- 20 23. The composition of claim 20 wherein the compatibilizer is a tBS-iB diblock or tBS-iB-tBS triblock copolymer having a GPC number average molecular weight of 50,000 to 200,000.
24. The composition of claim 20 wherein the isobutylene polymer (a) comprises a copolymer of isobutylene and para-methylstyrene.
- 25 25. The composition of claim 24 wherein the isobutylene polymer (a) is a halogenated copolymer of isobutylene and para-methylstyrene containing benzylic chlorine or bromine.
- 30 26. The composition of claim 20 wherein the olefinically unsaturated diene polymer is an elastomer selected from polybutadiene, synthetic

polyisoprene, natural rubber, elastomeric copolymers of butadiene with styrene or acrylonitrile, polychloroprene, or their mixtures.

27. A polymer blend wherein the composition of claims 20-26 is vulcanized,
cured, or cross-linked.
28. A method of forming a compatibilized polymer blend by combining:
- a) an isobutylene polymer selected from the group consisting of polyisobutylene, random copolymers of isobutylene with up to 10 weight % isoprene, halogenated random copolymers of isobutylene with up to 10 weight % isoprene, random copolymers of isobutylene with up to 20 weight % of a para-alkylstyrene, halogenated random copolymers of isobutylene and up to 20 weight % of a para-alkylstyrene and mixtures thereof;
 - b) at least one olefinically unsaturated diene polymer; and
 - c) a compatibilizer for components (a) and (b) comprising a block-graft copolymer of at least one recurring polyisobutylene segment and at least one recurring segment comprising a C₄ to C₆ alkyl ring substituted styrene or ring-substituted alpha-methylstyrene.
29. The method of claim 28 wherein the compatibilizer comprises a copolymer of isobutylene and para-t-butylstyrene.
30. The method of claim 29 wherein the compatibilizer comprises a tbS-iB diblock copolymer or a tbS-iB-tbS or iB-tbS-iB triblock copolymer having a GPC number average molecular weight of 10,000 to 500,000 and that contains at least 10 weight % of para-t-butylstyrene.
31. The method of claim 20 wherein components (a) and (b) are present at 95-5 parts by weight of (a) per 5-95 parts by weight of (b).

32. The method of claim 31 wherein the compatibilizer is present at 2 to 20 weight % based on the blend polymer content.
- 5 33. The method of claim 32 wherein the compatibilizer is a tBS-iB diblock or tBS-iB-tBS triblock copolymer having a GPC number average molecular weight of 50,000 to 200,000.
34. The method of claim 28 wherein the isobutylene polymer (a) comprises a copolymer of isobutylene and para-methylstyrene.
- 10 35. The method of claim 34 wherein the isobutylene polymer (a) is a halogenated copolymer of isobutylene and para-methylstyrene containing benzylic chlorine or bromine.
- 15 36. The method of claim 28 wherein the olefinically unsaturated diene polymer is an elastomer selected from polybutadiene, synthetic polyisoprene, natural rubber, elastomeric copolymers of butadiene with styrene or acrylonitrile, polychloroprene, or their mixtures.
- 20 37. The method of claims 28-36, further comprising a vulcanizing, cross-linking, or curing step.

1/2



2/2

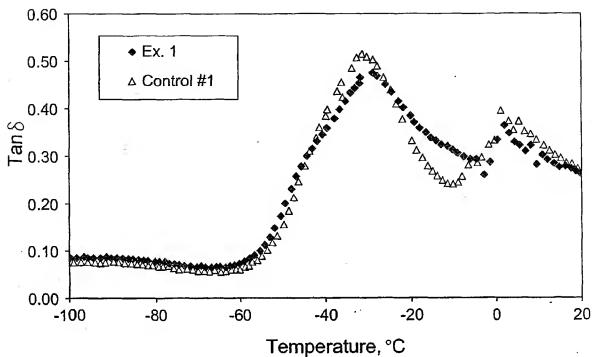


Fig. 2

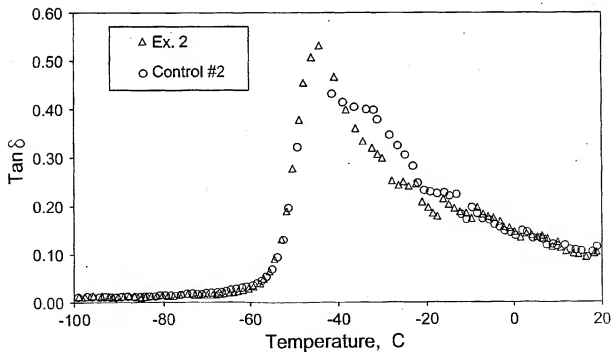


Fig. 3

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
25 April 2002 (25.04.2002)

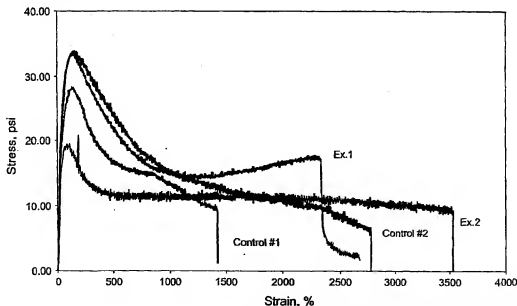
PCT

(10) International Publication Number
WO 02/032994 A3

- (51) International Patent Classification: C08L 23/22, 23/28, 21/00
- (21) International Application Number: PCT/US01/31620
- (22) International Filing Date: 11 October 2001 (11.10.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/688,425 16 October 2000 (16.10.2000) US
- (71) Applicant (for all designated States except US): EXXON-MOBIL CHEMICAL PATENTS INC. [US/US]: 5200 Bayway Drive, Baytown, TX 77520-5200 (US).
- (72) Inventors: and
- (75) Inventors/Applicants (for US only): TSE, Mun, Fu [US/US]: 1706 Fair Oaks Drive, Seabrook, TX 77586 (US). WANG, Hsien-Chang [US/US]: 536 College, Bel-Aire, TX 77401 (US). KRISHNAMOORTI, R. [US/US]: 2412 Yorktown #312, Houston, TX 77056 (US). TSOU, Andy, H. [US/US]: 3007 Prairie Knoll Court, Houston, TX 77059 (US).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

[Continued on next page]

(54) Title: POLYMER BLEND COMPATIBILIZATION USING ISOBUTYLENE-BASED BLOCK COPOLYMERS



(57) Abstract: Compatibilized blends of an isobutylene polymer and an unsaturated diene polymer are prepared using a compatibilizing agent comprising a block-graft copolymer containing polyisobutylene segments and C_4 to C_6 alkyl-substituted styrene polymer segments, such as poly(*t*-butylstyrene) segments.

WO 02/032994 A3



(88) Date of publication of the international search report:
4 July 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 01/31620

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/22 C08L23/28 C08L21/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 07451 A (EXXON CHEMICAL PATENTS INC) 30 May 1991 (1991-05-30)	1,9,28, 36
Y	page 3A, line 1 - page 4, line 10; claims 1,7,21,24	2-8, 10-27, 29-35
Y	US 4 946 899 A (KENNEDY JOSEPH P ET AL) 7 August 1990 (1990-08-07) cited in the application	2,3,6-8, 10-12, 15-20, 23-27, 29,30, 33-35
Y	column 11, line 38 - line 41; example 8 EP 0 691 378 A (BAYER AG) 10 January 1996 (1996-01-10) cited in the application page 3, line 10 - line 18; claim 1	4,5,13, 14,21, 22,31,32

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier document but published on or after the international filing date

'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

'O' document referring to an oral disclosure, use, exhibition or other means

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'Z' document member of the same patent family

Date of the actual completion of the international search

26 April 2002

Date of mailing of the international search report

07/05/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Clemente Garcia, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. onal Application No

PCT/US 01/31620

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9107451	A	30-05-1991	AT 143981 T 15-10-1996
			AU 4658389 A 28-04-1991
			BR 8907906 A 21-07-1992
			BR 8907907 A 21-07-1992
			CA 2003738 A1 03-04-1991
			CA 2009681 A1 03-04-1991
			DE 68927328 D1 14-11-1996
			DE 68927328 T2 20-02-1997
			EP 0497758 A1 12-08-1992
			EP 0501957 A1 09-09-1992
			ES 2092502 T3 01-12-1996
			JP 2957006 B2 04-10-1999
			JP 5500232 T 21-01-1993
			JP 3259054 B2 18-02-2002
			KR 154878 B1 01-12-1998
			WO 9107451 A1 30-05-1991
			WO 9104992 A1 18-04-1991
			US 5430118 A 04-07-1995
			US 5426167 A 20-06-1995
			US 5459174 A 17-10-1995
US 4946899	A	07-08-1990	US 5548023 A 20-08-1996
			US 5548029 A 20-08-1996
EP 0691378	A	10-01-1996	US 5162445 A 10-11-1992
			US 5654379 A 05-08-1997
			US 5824717 A 20-10-1998
			US 6013727 A 11-01-2000
			US 5959049 A 28-09-1999
US 4946899	A	07-08-1990	WO 9111468 A1 08-08-1991
			US RE34640 E 14-06-1994
EP 0691378	A	10-01-1996	DE 4424070 A1 11-01-1996
			EP 0691378 A2 10-01-1996
			JP 8048864 A 20-02-1996